



Degradation of VOC gases in liquid phase by photocatalysis at the bubble interface

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ABSTRACT

Photocatalytic reactions in the gas phase have a number of disadvantages including the adverse effects of relative humidity, the emission of decomposition intermediates at the reactor exit and the deactivation of the photocatalyst surface by decomposition intermediates. In this study, these disadvantages can be overcome using a novel photocatalytic reaction system. Volatile organic compound (VOC) gases were decomposed at the bubble interface in a TiO₂ suspension by using TiO₂ photocatalysis in the heterogeneous liquid-bubble (LB) phase since the intermediates dissolve into water and then are continuously decomposed regardless of humidity. Toluene, *p*-xylene, styrene and formaldehyde were chosen as model VOC gases to investigate photocatalytic reactivity in the LB phase. The removal ratio of VOC gases in the LB phase was equal to or greater than that in the gas phase, although the reactivity in the LB phase depended on the reaction rate of OH radicals and the hydrophobicity of the VOC gases. The reaction in the LB phase also depended on the wavelength and intensity of UV light. Specifically, the removal and mineralization ratios were improved by using shorter wavelengths of UV irradiation. Finally, as a trial experiment, we applied the microbubble technique to this system. When VOC gases were introduced into the system as microbubbles, VOC gas was effectively removed and high removal ratios were obtained regardless of the wavelength and intensity UV light.

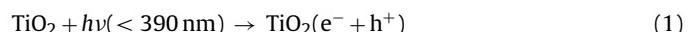
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1. Introduction

Volatile organic compounds (VOCs) are common air pollutants and can be found in both outdoor and indoor environments. Many VOCs are known to be toxic and considered to be carcinogenic. Some of these compounds are associated with sick building syndrome (SBS), which causes symptoms including mucous membrane irritation, headache and fatigue [1,2]. The most significant problem posed by VOCs is their potential role in photochemical reactions in the atmosphere, which contributes to the generation of pollutants. Photocatalytic oxidation is considered to be a promising method for the treatment and decomposition of VOCs to final products such as H₂O and CO₂, and titanium dioxide (TiO₂) has been used as a photocatalyst for UV-induced photocatalytic reactions. These reactions are highly attractive because they do not require high temperatures

and the catalyst can be used almost indefinitely. In recent years, a number of reports have been published detailing work done in this field [3–7].

The gas phase degradation of pollutants by TiO₂ mainly occurs via oxidative decomposition by OH radical, which can be generated from water under ultraviolet (UV) irradiation (<390 nm) in the presence of TiO₂, as shown in Eqs. (1)–(3) [8–10].



In the above photocatalytic reactions, high reaction efficiency can be achieved; however, the dependency of the reactions on relative humidity remains high [11,12]. Moreover, intermediate products of degradation are formed [13,14] that can adsorb onto the surface of the catalyst causing deterioration of the catalyst [15,16], due to which the reaction cannot proceed to completion. To realize effective photocatalysis, it is necessary to reduce the adsorption of intermediate products onto the catalyst surface and to achieve high reaction efficiency. To address these issues, we propose photocatal-

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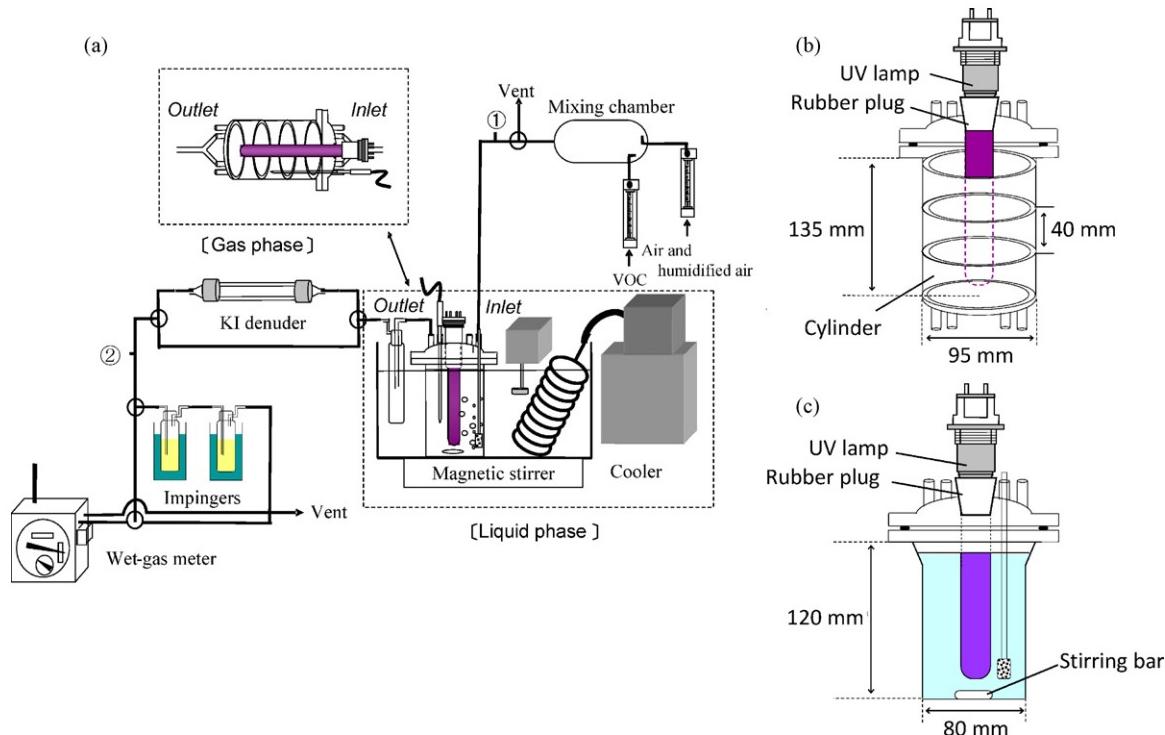


Fig. 1. (a) Schematic diagram of experimental setup. (b) Gas-phase photoreactor. (c) LB-phase photoreactor.

ysis using short-wavelength UV light to decompose pollutants, as well as treatment of decomposition intermediates by using an air washer with a water spray [17–20]. In these previous studies, the decomposition intermediates of VOCs have been shown to be water soluble and readily trapped in water.

Based on these observations, we propose the introduction of VOCs as bubbles into a TiO₂ suspension. If VOC degradation by photocatalysis can be effectively realized in the heterogeneous liquid-bubble (LB) phase, the decomposition intermediates could be dissolved into water. In addition, the catalyst in water could be self-cleaned, which would alleviate adsorption of decomposition intermediates onto the surface of the catalyst. Self-cleaning of the catalyst in water would allow decomposition of VOCs to be maintained at a constant rate and the produced intermediates to be decomposed.

Recently, a study on the decomposition of VOCs by Fenton's reaction, which uses a mechanism similar to VOC injection into water, has been reported [21]. However, in this reaction, the dependency on H₂O₂ concentration is high. Therefore, the decomposition of VOCs using UV light with TiO₂ would be advantageous compared with Fenton's reaction from the perspective of continuous treatment.

In this study, VOCs were introduced into a TiO₂ suspension as bubbles under UV light to decompose the VOCs in the LB phase and to trap the produced intermediates in water, thus allowing continuous decomposition. The VOC removal and mineralization ratios in the LB phase were assessed in comparison with the photocatalysis in the gas phase using TiO₂ and UV light. Furthermore, parameters that affect the decomposition process such as the gas species, UV wavelength, light intensity, bubble size and reduction of intermediates were also evaluated. In particular, microbubbles (MBs), which are defined as bubbles with a diameter less than 50 µm [22], were used as an improved means of introducing VOCs, since MBs in water have a number of advantageous properties, such as the high solubility of the encapsulated gas into water [23], a relatively low rising rate (e.g., 56 µm/s for MBs of 10 µm [24]) and high diffusivity

based on repulsion by negative charges [25]. This paper describes a novel process for effectively applying MBs and presents data on the photocatalytic treatment of organic gaseous pollutants in the LB phase.

2. Experimental

2.1. Reactor

A schematic diagram of the experimental setup for the decomposition of VOCs is shown in Fig. 1(a); the gas-phase and LB-phase photoreactors are shown in Fig. 1(b) and (c), respectively. Degussa P-25 TiO₂ photocatalyst (Nippon Aerosil) was used in all experiments since P-25 TiO₂ particles can generate a high number of OH radicals in the liquid phase [26]; thus, a valid comparison of the photocatalytic reaction in the gas and LB phases can be made. The crystal structure of the P-25 TiO₂ particles was approximately 80% anatase and 20% rutile, and the average particle diameter was 30 nm. The surface area of TiO₂ measured with a BET surface analyzer (Micromeritics, Flowsorb III-2305) was 50 m²/g [27,28].

The gas-phase reactor was composed of Pyrex glass (volume: 0.95 L). The inside wall of the reactor consisted of three inner cylinders. The UV lamp was located at the center of the reactor. The surface of the inner wall of the reactor was uniformly coated with P-25 TiO₂ particles (about 0.010 g) by dipping. On the other hand, the LB-phase reactor had the same shape as the gas-phase reactor, but the volume of the Pyrex glass was 0.60 L. To assess only the photocatalytic reaction in the LB phase, UV lamp for illuminating the TiO₂ suspension was wrapped with aluminum foil and Teflon tape. Milli-Q water (400 mL) and P-25 TiO₂ particles (0.75 g/L) were loaded into the reactor as an optimal condition. The VOCs were introduced into the TiO₂ suspension through a glass filter (GF) which generated millimeter-scale bubbles. The apparatus used for the application of MBs to the photocatalytic decomposition of VOCs in the LB phase is shown in Fig. 2. The same type of UV lamp was used with the MB reactor as with the LB-phase reactor. The effects of light intensity

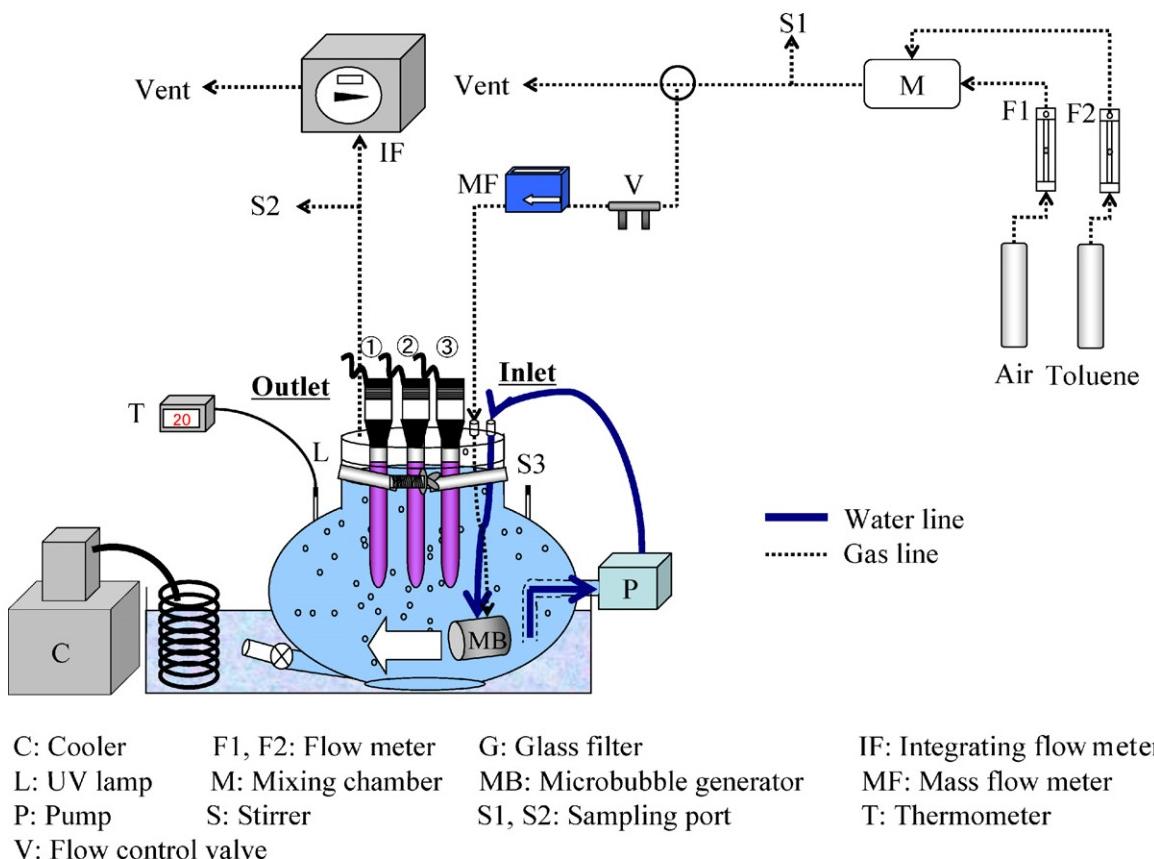


Fig. 2. Schematic diagram of experimental setup for MB application.

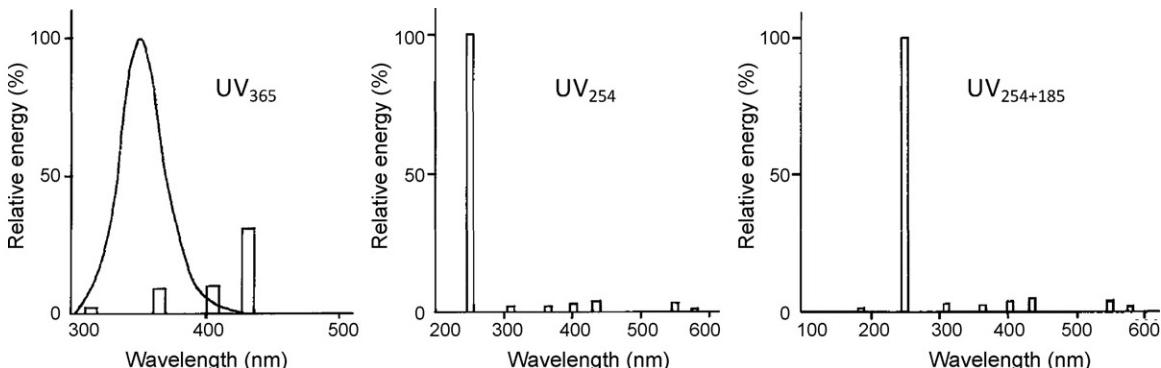


Fig. 3. Emission spectra of three types of UV lamps.

were studied by changing the number of lamps. When the reactor was equipped with one lamp, the lamp was installed at position 2, and lamps were installed at positions 1–3 when three lamps were installed, as shown in Fig. 2. Milli-Q water (6.0 L) and P-25 TiO₂ particles (0.75 g/L) were loaded into the reactor. The VOC gases were introduced into the TiO₂ suspension as MBs with diameters less than 15 μm by using a high-speed rotating MB generator that was placed in the reactor.

2.2. UV sources

The output power (8 W) was the same for all three types of UV lamps, which operated at different wavelengths (Sankyo Denki, FLK8MQ series). The main wavelengths were 365 nm (UV₃₆₅), 254 nm (UV₂₅₄) and 254 nm with 3% of the output power at 185 nm (UV₂₅₄₊₁₈₅). The emission spectra of the lamps are shown in Fig. 3.

2.3. Generation of VOC and formaldehyde gases

In order to investigate the effects of various VOC species on photocatalytic reactivity in the LB phase, various VOC gases such as toluene, *p*-xylene, styrene and formaldehyde were chosen and used in the degradation experiment. Table 1 shows the properties of

Table 1

Adsorption wavelength, octanol/water partition coefficient and reaction rates with OH radical and O₃ for VOC and formaldehyde gases.

Parameter	Toluene	<i>p</i> -Xylene	Styrene	Formaldehyde
Adsorption wavelength (nm)	260	—	244	360
$\log P_{OW}$	2.7	3.2	3.2	0.35
$k_{OH^{\cdot}} \times 10^{-12}$	8.5	12	100	0.20
$k_{O_3} \times 10^{-19}$	0.12	0.0040	170	0.000021

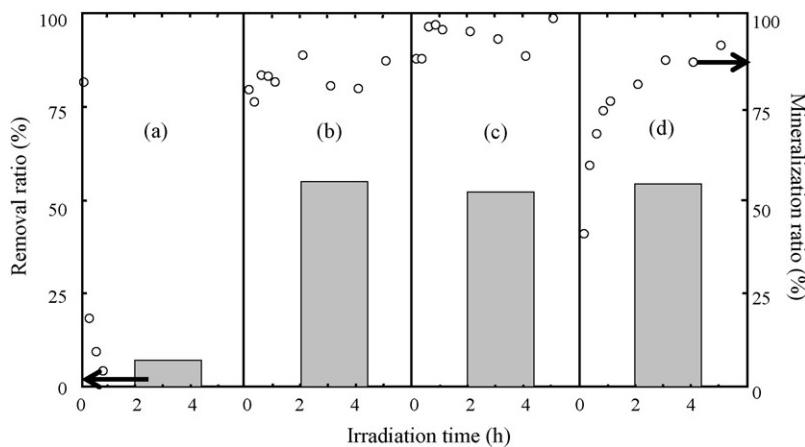


Fig. 4. Toluene removal and mineralization ratios under various experimental conditions. (a) Gas phase (R.H. 1–2%), (b) gas phase (R.H. 50–60%), (c) gas phase (R.H. 70–80%), (d) LB phase. $[C_7H_8]_0$: 5 ppm; UV lamp: UV₃₆₅; flow rate: 1 L/min.

the gases, namely, the adsorption wavelength, octanol/water partition coefficient and reaction rates with OH radical and ozone (O_3) [29,30].

Standard VOCs (toluene, *p*-xylene, and styrene) from gas cylinders were diluted with clean dry air ($H_2O < 10$ ppm) to obtain arbitrarily chosen concentrations and supplied to a reactor. Standard formaldehyde, which was prepared from paraformaldehyde powder by sublimation in a thermostatic bath, was exposed to a stream of dry air for stable gas generation. The concentration of formaldehyde was adjusted to approximately 16 ppm. Humidified air generated from a humidifier, which was filled with Milli-Q water and constructed from a PTFE tube with dry air, was used to adjust the relative humidity of the standard gases before introducing them into a reactor. The relative humidity of the introduced gases ranged from 1% to 80%.

2.4. Experimental procedure and analysis

After checking the reactor temperature (20 ± 2 °C), a reaction was started by introducing 0.25 or 5.0 ppm of VOC gas into a reactor at 1 L/min under UV irradiation as shown in Fig. 1(a). The variation in the amount of gas introduced over time was checked by measuring the concentrations at sampling ports (1) and (2), as shown in Fig. 1(a). The concentrations of the VOC gases and the decomposition products (CO and CO_2) were determined with a gas chromatograph equipped with flame ionization detection (GC-

FID; GL Sciences, GC-390B) and with a GC-FID (Shimadzu, GC-15A) equipped with a methanizer (GL Sciences, MT-221), respectively. Removal and mineralization ratios were calculated using the following equations:

$$\text{removal ratio}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (4)$$

$$\text{mineralization ratio}_{\text{toluene}}(\%) = \frac{C_{CO_2,t} + C_{CO,t}}{(C_0 - C_t) \times 7} \times 100 \quad (5)$$

$$\text{mineralization ratio}_{\text{formaldehyde}}(\%) = \frac{C_{CO_2,t} + C_{CO,t}}{C_0 - C_t} \times 100 \quad (6)$$

Here, the upstream initial concentration is C_0 , the downstream concentration at time t is C_t , and the CO_2 and CO concentrations at time t are $C_{CO_2,t}$ and $C_{CO,t}$. Formaldehyde gas was measured with a high-performance liquid chromatograph equipped with an ultraviolet detector (HPLC-UV; Shimadzu, LC-9A) after derivatization with 2,4-Dinitrophenylhydrazine (DNPH), and water-soluble organic compounds (WSOCs) were measured with a total organic carbon (TOC) analyzer (Shimadzu, TOC-V). As O_3 was formed in the experiment using UV₂₅₄₊₁₈₅, O_3 was measured with a UV-absorption ozone analyzer (Shimadzu, UVAD-1000) and removed by a denuder with potassium iodide (KI) when the VOC gases were introduced into the GC-FID because O_3 causes serious damage to GC columns [31]. Furthermore, fine particles were generated as the decomposition intermediates under UV₂₅₄₊₁₈₅ irradiation. These

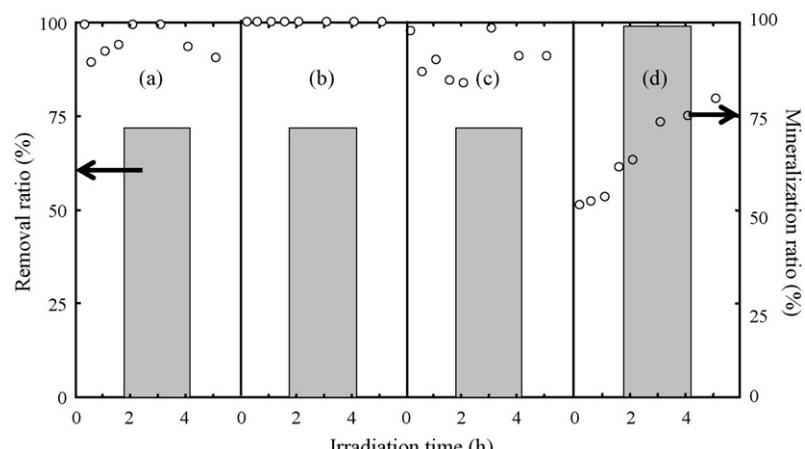


Fig. 5. Formaldehyde removal and mineralization ratios under various experimental conditions: (a) gas phase (R.H. 1–2%), (b) gas phase (R.H. 50–60%), (c) gas phase (R.H. 70–80%), (d) LB phase. $[HCHO]_0$: 16 ppm; UV lamp: UV₃₆₅; flow rate: 1 L/min.

Table 2WSOC and formaldehyde concentrations in gas stream collected in water impingers at the outlet of the reactor^a.

Conditions	Removal ratio (%)	WSOC concentration (mg/L)	Formaldehyde concentration (mg/L)
Gas phase	55	51.4 ± 1.5	6.17 ± 1.2
LB phase	53	20.6 ± 0.85	0.15 ± 0.09

[C₇H₈]₀: 5 ppm; UV lamp: UV₃₆₅; R.H.: 50–60% (gas phase).^a Collection gas velocity: 1 L/min; water volume in impinger: 5 mL; total volume of gas collected: 600 L.

were measured with a scanning mobility particle sizer (SMPS; TSI, Model-3934) at the reactor outlet.

Toluene was used as a model VOC gas to investigate the effects of MBs (Fig. 2). The concentration of toluene gas was adjusted to 5 ppm, and toluene was introduced at 0.2 L/min into a reactor either as millimeter-scale bubbles through GF or as MBs though the MB generator. The effects of MB were evaluated based on the removal ratio of decomposition products and intensity of UV light.

3. Results and discussion

3.1. Gas-phase reaction

Relative humidity is an important parameter for comparing the photocatalytic decomposition efficiency of the gas and LB phases. It is thought that high relative humidity can be a source of OH radical production but lowers activity by coating the catalyst with the water that condenses due to excessive humidity [3,4]. In particular, the properties of the pollutant gas are critical for achieving high reaction efficiency since these characteristics affect competitive adsorption between the pollutant and water molecules on the catalytic surface. Therefore, toluene and formaldehyde gases, which have different octanol–water partition coefficients, were used in the photocatalytic reaction to evaluate the effects of relative humidity. Removal and mineralization ratios in terms of various experimental parameters for toluene and formaldehyde in the gas and LB phases are shown in Figs. 4 and 5, respectively. The removal ratio of toluene was 7% when relative humidity was between 1% and 2%, while the removal and mineralization ratios were 53% and sometimes above 75% when relative humidity ranged from 50% to 60% and from 70% to 80%, respectively (Fig. 4). It was found that the water contributes effectively to radical production and reactivity. Similar findings have been reported previously [32,33]. On the other hand, the removal ratio of formaldehyde was different from that of toluene. The effects of relative humidity were not observed under the three conditions investigated (relative humidity: 1–2%, 50–60% and 70–80%), resulting in a removal ratio of 72% and a total mineralization ratio of about 93%. It was found that the decomposition of VOCs can be strongly affected by relative humidity, while the decomposition of formaldehyde was not affected. These results agree with the previously reported finding that the bond energies of toluene and formaldehyde differ on a TiO₂ surface in the presence of a hydroxyl group [5,34].

3.2. LB-phase reaction

The same experiment that was presented in Section 3.1 for gas phase was carried out for the LB phase. The results obtained for the gas-phase reaction are compared and discussed in this section. The removal ratio of toluene was approximately 50%, which was similar to the observed removal ratio in gas-phase reaction, while the removal ratio of formaldehyde was almost 100%, as shown in Figs. 4 and 5. These results indicate that toluene was removed effectively in the LB phase by the photocatalytic reaction, and it is believed that sufficient OH radicals were generated from water

at the stable relative humidity under the reaction conditions. Due to the high hydrophilicity of formaldehyde, a high removal ratio could be achieved, indicating that formaldehyde could be efficiently trapped in the TiO₂ suspension. The mineralization ratios of toluene and formaldehydes were 80% and 63%, respectively. The mineralization ratio in the LP phase was lower than that in the gas phase; however, the actual mineralization ratio is possibly higher due to dissolution of CO₂ into water.

The observed mineralization ratios of formaldehyde were found to be lower than those of toluene in our results. The reason for the lower mineralization ratio of formaldehyde could be explained by gaseous formaldehyde changing to a liquid phase by dissolving into water easily, and resulting homogeneous reaction occurring in the liquid phase. Thus, decomposition of formaldehyde could be difficult in the LB phase. However, the mineralization ratio of toluene and formaldehyde increased as a function of time, which indicated that mineralization progress continued in the TiO₂ suspension solution.

The photocatalytic reaction in the LB phase produced active species in an aqueous medium and yielded results that were equal to or better than those found of the gas-phase reaction. Therefore, this LB-phase reaction can be effectively used for the decomposition of VOCs.

3.3. Emission of decomposition intermediates under UV₃₆₅ irradiation

Not only the photocatalytic decomposition of toluene in the gas (R.H. 50–60%) and LB phases under UV₃₆₅ irradiation, but also the emission of decomposition intermediate products from the outlet of the reactor was investigated. Reaction time was set as 10 h; over the course of the reaction, the exhaust gas was trapped by an impinger containing Milli-Q water for the analysis of WSOCs and formaldehyde which were intermediate products of toluene decomposition. The results for the collected intermediate products of toluene are listed in Table 2. Removal ratios in the gas- and LB-phase reactions were similar, while the collected WSOC and formaldehyde concentrations in the LB-phase reaction were lower than those in the gas phase, resulting in drastically reduced emission of decomposition intermediate products. These results indicate that photocatalytic decomposition of VOCs in the LB phase is highly practical for application to VOC decomposition.

3.4. Evaluation of photocatalytic reaction in LB phase

As previously discussed in Section 3.3, removal efficiency that was equal to or greater than that of the gas-phase reaction was observed for the photocatalytic reaction in the LB phase. This result was primarily due to the effective production of active species. Furthermore, the concentration of intermediate products in the reaction mixture was reduced since the intermediates were emitted to the outlet of the reactor. To evaluate the LB-phase reaction, the effects of the wavelength of UV light, the initial VOC concentration, and the identity of the VOC gas species were investigated further.

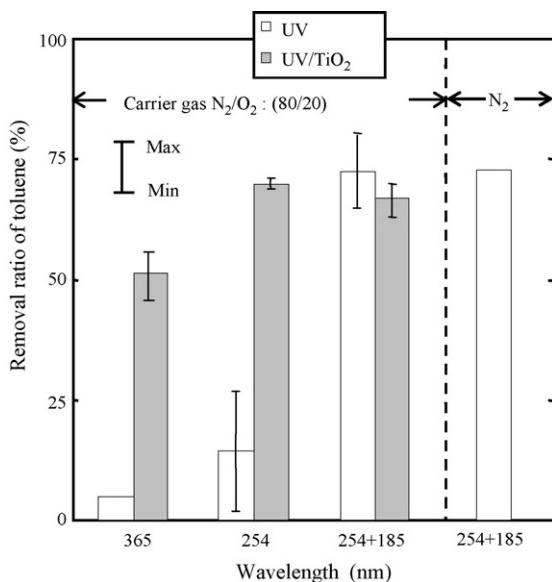
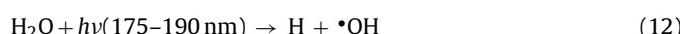
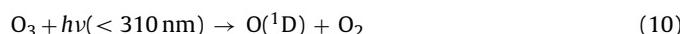
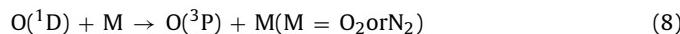
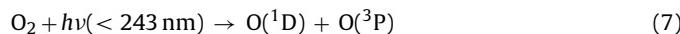


Fig. 6. Toluene removal ratios for different carrier gases and UV wavelengths with or without TiO₂. [C₇H₈]₀: 5 ppm; flow rate: 1 L/min.

3.4.1. Effects of wavelength of UV light

Three different UV sources, namely, UV₃₆₅, UV₂₅₄ and UV₂₅₄₊₁₈₅, were used for the photocatalytic degradation of toluene gas in the LB phase in order to examine the effects of various UV wavelengths. The results under the different carrier gases and UV wavelengths with or without TiO₂ mixing are shown in Fig. 6. First, photodegradation of toluene under UV irradiation without TiO₂ was examined. Under UV₂₅₄₊₁₈₅ irradiation, the removal ratio improved significantly compared with the other UV conditions in the LB-phase reaction. Not only direct photodegradation of VOC gas occurred, but also production of ozone and OH radical, which have been reported for UV₂₅₄₊₁₈₅ irradiation in the gas phase, as shown in the following equations [17,35]:



However, when ozone concentration was measured at the outlet of the reactor for the LB phase under UV₂₅₄₊₁₈₅ irradiation, ozone production was hardly observed (20–50 ppb). Based on this result, the contribution of direct photolysis and ozone degradation, as occurs in the gas phase, were found to be lower for VOC decomposition by the LB-phase reaction. The same removal ratio was observed under N₂ aeration, conditions under which ozone is not produced, indicating again that the role of ozone was insignificant in the LB-phase reaction as shown in Fig. 6. It was possible to improve the decomposition of VOC considerably in the LB phase by generating abundant OH radicals from water with short-wavelength 185-nm UV light (Eq. (11)) when UV₂₅₄₊₁₈₅ lamp was used.

Second, the effects of different UV wavelengths in the presence of the photocatalyst were examined. Fig. 6 shows the elevated removal ratios in accordance with TiO₂ addition under UV₃₆₅/TiO₂, and UV₂₅₄/TiO₂ conditions. It was found that toluene inside of bubbles was removed effectively, producing active species that arise from photocatalytic reaction at the bubble interface in the LB phase. On the other hand, TiO₂ addition was found to have

Table 3

Toluene removal and mineralization ratios under UV₂₅₄₊₁₈₅ irradiation with or without TiO₂ photocatalyst.

Conditions	Removal ratio (%)	Mineralization ratio (%)
UV ₂₅₄₊₁₈₅ /TiO ₂	74	78
UV ₂₅₄₊₁₈₅	74	49

[C₇H₈]₀: 5 ppm, flow rate: 1 L/min.

no effect on the removal ratio under UV₂₅₄₊₁₈₅ irradiation while the mineralization under UV₂₅₄₊₁₈₅/TiO₂ conditions was markedly increased compared with UV₂₅₄₊₁₈₅ irradiation without TiO₂ addition, as shown in Table 3. It was possible to increase the production of active species using a short-wavelength UV lamp to apply higher energy light to the LB phase. These results indicate that active species on the TiO₂ surface were effective for the degradation of VOCs as well as mineralization of decomposition intermediate products.

3.4.2. Generation of secondary organic aerosol (SOA)

The production of secondary organic aerosol (SOA) has not been observed under UV₃₆₅ and UV₂₅₄ irradiation. In case of UV₂₅₄₊₁₈₅ irradiation, it has been reported that a gas-to-particle conversion occurs via a photochemical reaction, producing SOA from the decomposition intermediates of VOC gas [17], although high removal and mineralization ratios have been obtained. In particular, ultrafine particles (D_p ≤ 100 nm) have been reported to have an adverse effect on human health [33].

When toluene was decomposed in the gas (R.H.: 50–60%) and LB phases under UV₂₅₄₊₁₈₅/TiO₂ conditions, the size distribution of the produced SOA was measured at the outlet of the reactor (Fig. 7). High particle concentrations on the order of 10⁵ were observed due to SOA production for the gas-phase reaction, while low particle concentrations on the order of 10³ were observed for the LB-phase reaction, which is lower than the typical particle number concentration under ambient atmospheric conditions. The decreased formation of SOA depended on the trapping of not only newly formed SOA but also water-soluble precursors in the TiO₂ suspension. It was possible to achieve high removal and mineralization ratios for the decomposition of VOCs in the LB phase using short-wavelength UV irradiation by reducing gaseous and particulate decomposition intermediates.

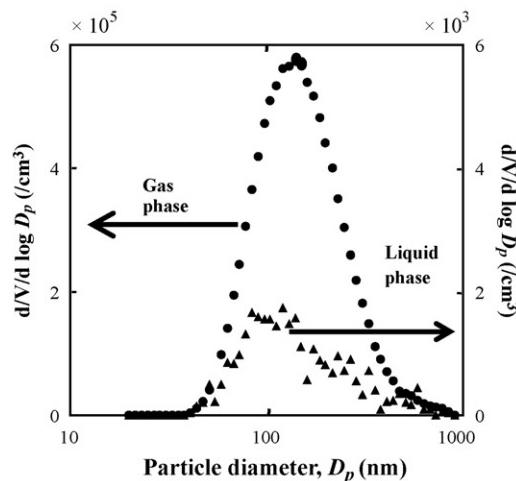


Fig. 7. Size-divided number concentration (N) of SOA measured at the outlet of gas-phase reactor or LB-phase reactor. R.H.: 50–60%; [C₇H₈]₀: 5 ppm; UV lamp: UV₂₅₄₊₁₈₅; flow rate: 1 L/min.

Table 4

Toluene removal ratios under irradiation of three types of UV lamps with TiO_2 photocatalyst.

Conditions	Concentration (ppm)	Removal ratio (%)
$\text{UV}_{254+185}/\text{TiO}_2$	5.0	74
	0.25	78
$\text{UV}_{254}/\text{TiO}_2$	5.0	75
	0.25	77
$\text{UV}_{365}/\text{TiO}_2$	5.0	53
	0.25	79

Flow rate: 1 L/min.

3.4.3. Influence of initial concentration

To clarify the effects of VOC gas concentration, an experiment examining the decomposition of toluene was performed at high (5.0 ppm) and low (0.25 ppm) concentrations. In addition, various UV lamps (UV_{365} , UV_{254} and $\text{UV}_{254+185}$) were used to observe the effects of UV wavelength. The results are shown in Table 4. Under $\text{UV}_{365}/\text{TiO}_2$ conditions, the removal ratio for the low initial concentration was higher than that for the high initial concentration. This result indicates that the amount of active species in both cases was similar in the LB phase, and that the toluene frequently came into contact with active species at a low toluene concentration when considering the higher removal ratio.

There was no difference for removal ratios between initial concentration of 0.25 and 5.0 ppm under $\text{UV}_{254}/\text{TiO}_2$ and $\text{UV}_{254+185}/\text{TiO}_2$ conditions. As shown in Fig. 3, the UV_{254} and $\text{UV}_{254+185}$ lamps had line spectrum. Therefore, the amount of active species present was sufficient because the photocatalyst could absorb light emission effectively. Although there would be no difference between the use of the UV_{254} and $\text{UV}_{254+185}$ lamps in terms of removal ratio, it would be more desirable to use the $\text{UV}_{254+185}$ lamp to mineralize VOC quickly as discussed in Section 3.4.1. However, it would be difficult to improve removal ratio further by increasing the concentration of active species. These results show that the LB-phase reaction depended strong on the likelihood of VOC gas coming into contact with active species, and necessary to focus on how to increase contact probability between active species and VOC gas.

3.4.4. Effects of different VOC gases

To examine the effects of various VOC gas species on photocatalytic decomposition in LB phase, three VOC gases were used under $\text{UV}_{254}/\text{TiO}_2$ and $\text{UV}_{254+185}/\text{TiO}_2$ conditions. The VOC gases (toluene, *p*-xylene and styrene; see Table 1) with differing octanol–water partition coefficients and reaction rates with OH radical as well as ozone were used. The results are shown in Fig. 8.

Although the reaction rate of *p*-xylene with OH radical is higher than that of toluene, the removal ratios of *p*-xylene were lower than those of toluene under $\text{UV}_{254}/\text{TiO}_2$ and $\text{UV}_{254+185}/\text{TiO}_2$ conditions. This indicates that hydrophobic substances such as *p*-xylene are less likely to come into contact with an active species in the LB phase since the reaction occurs at the bubble interface. The low removal ratio of *p*-xylene indicates that it is difficult for highly hydrophobic substances to reside at the bubble interface. Therefore, improving the likelihood of contact between active species and the VOC gas is essential. However, styrene had a removal ratio that was 10% higher than that of *p*-xylene, even though the octanol–water partition coefficient of the two is almost the same. This indicates that the removal ratio is decided by the reaction rate with OH radical when hydrophobicity is similar.

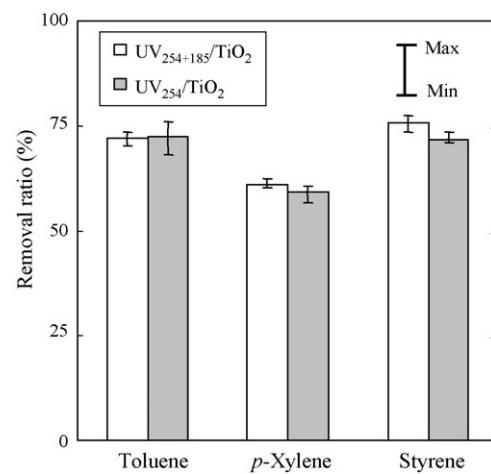


Fig. 8. Removal ratios for various VOC gases with TiO_2 and two different UV lamps. $[\text{C}_7\text{H}_8]_0$: 5 ppm; $[\text{p-C}_8\text{H}_{10}]_0$: 5 ppm; $[\text{C}_8\text{H}_8]_0$: 5 ppm; flow rate: 1 L/min.

3.5. Application of MB technique to BL-phase reaction

It is necessary to improve the likelihood of contact at the bubble interface between VOCs and the active species produced by the photocatalyst to obtain higher removal ratios and realize the practical application of this method. Therefore, the MB technique, which can generate much smaller bubbles of VOC gas, was used. The removal ratios of toluene using GF and MBs under $\text{UV}_{254}/\text{TiO}_2$ and $\text{UV}_{254+185}/\text{TiO}_2$ conditions are shown in Fig. 9. In addition, the effects of light intensity (one or three lamps) and UV wavelength (254 nm or 365 nm) are shown in Table 5. The removal ratio was improved considerably when MBs were used compared with GF millimeter-scale bubbles. A removal ratio of 98% for toluene gas was obtained under MB/ $\text{UV}_{254}/\text{TiO}_2$ conditions with three UV lamps. On the other hand, 55% of removal ratio was obtained even under MB/ TiO_2 conditions without UV irradiation indicating that toluene gas was effectively trapped in water due to the lower rising rate of MBs in the water [24]. Therefore, a high removal ratio could be achieved because the likelihood of contact between toluene gas and the active species formed by the TiO_2 photocatalyst was improved.

The difference in the removal ratio between one and three lamps was 7% under MB/ $\text{UV}_{254}/\text{TiO}_2$ conditions, while this difference was

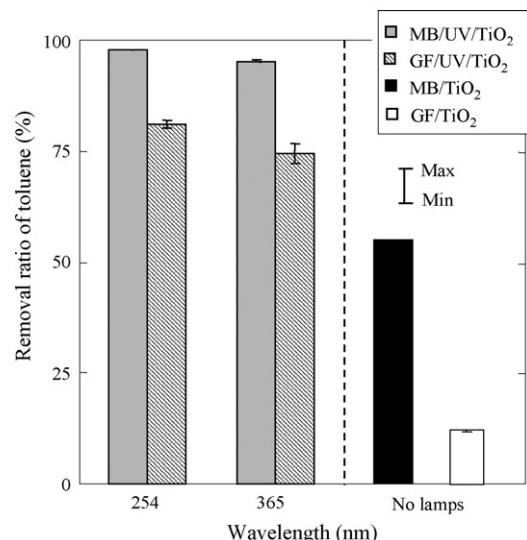


Fig. 9. Toluene removal ratio under several reaction conditions. Flow rate: 0.20 L/min.

Table 5

Influence of wavelength and number of UV lamps under conditions of MB application.

Experimental conditions		Removal ratio (%)
Conditions	Number of UV lamps	
MB/UV ₂₅₄ /TiO ₂	1	91
	3	98
MB/UV ₃₆₅ /TiO ₂	3	95
GF/UV ₂₅₄ /TiO ₂	1	49
	3	81
GF/UV ₃₆₅ /TiO ₂	3	74

[C₇H₈]₀: 5 ppm; flow rate: 0.2 L/min.

about 30% under GF/UV₂₅₄/TiO₂ conditions. The difference in the removal ratio between MB/UV₂₅₄/TiO₂ and MB/UV₃₆₅/TiO₂ conditions was 3%, while the difference in the removal ratio between GF/UV₂₅₄/TiO₂ and GF/UV₃₆₅/TiO₂ was 7%. These results show that a sufficient removal ratio can be achieved at lower light intensity and longer UV wavelengths under MB/UV/TiO₂ conditions because of the higher likelihood of contact between VOCs and the active species formed by the TiO₂ photocatalyst. Therefore, high reaction efficiency of VOC decomposition can be obtained regardless of wavelength at lower light intensity using the MB technique and a reactor for VOC decomposition was designed that was efficient in terms of cost and energy.

4. Conclusions

The effectiveness of VOC gas degradation by photocatalysis in the LB-phase and an application of a new air purification technique are presented in this study. The results of this work are summarized as follows:

- At the bubble interface, OH radicals produced from water could be effectively utilized in the LB-phase reaction. As a result, the removal ratios for VOC degradation in LB-phase reactions were equal to or higher than those in gas-phase reactions.
- The removal ratio of VOC gas highly depended on the likelihood of contact between the VOC gas and the active species at the bubble interface, which is affected by the likelihood of the VOC residing at the bubble interface. Therefore, the removal ratio also depended on the hydrophobic properties of the VOC gas. In the case of VOCs with similar hydrophobicity, the removal ratio depended on their rate of reaction with OH radicals.
- Under UV₂₅₄ and UV₂₅₄₊₁₈₅ irradiation, which had line spectra, high removal ratios of VOC gas were obtained that were independent of VOC concentration. It was thought that sufficient active species were produced. In particular, mineralization of intermediate products to CO or CO₂ was promoted under UV₂₅₄₊₁₈₅ irradiation.
- Using the LB-phase reaction, water-soluble gaseous and particulate intermediates could be trapped, concentrated into water and the particle content in the exhaust at the outlet of the reactor

could be controlled. The problems of ozone and particle production could also be resolved even though the UV₂₅₄₊₁₈₅ lamp was used to improve the removal and mineralization ratios. From these results, it is possible to envision the development of a single reactor that would be sufficient for the decomposition of VOC gas as well as the treatment of decomposition intermediate products.

- By introducing VOC gas into the reactor as MBs, high reaction efficiency could be achieved by improving of the likelihood of contact between the VOC gas with active species in LB phase, regardless of UV wavelength and light intensity. This suggests that a reactor can potentially be designed for VOC decomposition that is highly efficient in terms of cost and energy.

References

- J.L. Repace, Environ. Int. 8 (1982) 21–36.
- M. Hodgson, H. Levin, P. Wolfson, J. Allergy Clin. Immunol. 94 (1994) 296–303.
- S.B. Kim, S.C. Hong, Appl. Catal. B: Environ. 35 (2002) 305–315.
- X. Deng, Y. Yue, Z. Gao, Appl. Catal. B: Environ. 39 (2002) 135–147.
- C.H. Ao, S.C. Lee, J.Z. Yu, J.H. Xu, Appl. Catal. B: Environ. 54 (2004) 41–50.
- K.P. Yu, G.W.M. Lee, Appl. Catal. B: Environ. 75 (2007) 29–38.
- J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, Atmos. Environ. 43 (2009) 2229–2246.
- C.S. Turchi, D.F. Ollis, J. Catal. 122 (1990) 178–192.
- C.-H. Wu, C.-H. Yu, J. Hazard. Mater. 169 (2009) 1179–1183.
- A.R. Khataee, M.N. Pons, O. Zahraa, J. Hazard. Mater. 168 (2009) 451–457.
- D.S. Tsoukliris, T. Maggos, C. Vassilakos, P. Falaras, Catal. Today 129 (2007) 96–101.
- T. Liu, F. Li, X. Li, J. Hazard. Mater. 152 (2008) 347–355.
- L. Cao, Z. Gao, S.L. Suib, T.N. Obee, S.O. Hay, J.D. Freihaut, J. Catal. 196 (2000) 253–261.
- M.C. Blount, J.L. Falconer, Appl. Catal. B: Environ. 39 (2002) 39–50.
- L. Cao, Z. Gao, S.L. Suib, T.N. Obee, S.O. Hay, J.D. Freihaut, J. Catal. 196 (2000) 253–261.
- E. Pierra, J.A. Ayllón, X. Doménech, J. Peral, Catal. Today 76 (2002) 259–270.
- J. Jeong, K. Sekiguchi, K. Sakamoto, Chemosphere 57 (2004) 663–671.
- J. Jeong, K. Sekiguchi, W. Lee, K. Sakamoto, J. Photochem. Photobiol. A: Chem. 169 (2005) 279–287.
- J. Jeong, K. Sekiguchi, M. Saito, Y. Lee, Y. Kim, K. Sakamoto, Chem. Eng. J. 118 (2006) 127–130.
- K. Sekiguchi, K. Yamamoto, K. Sakamoto, Catal. Commun. 9 (2008) 281–285.
- M. Tokumura, R. Nakajima, H.T. Znad, Y. Kawas, Chemosphere 46 (2008) 768–775.
- S. Lee, W. Sutomo, C. Liu, E. Loth, Int. J. Multiphase Flow 31 (2005) 706–722.
- B.A. Walker, C. Tsouris, W.D. DePaoli, T.K. Klassen, Ozone Sci. Eng. 23 (2001) 77–87.
- M. Takahashi, J. Phys. Chem. B 109 (2005) 21858–21864.
- M. Takahashi, T. Kawamura, Y. Yamamoto, H. Ohnari, S. Himuro, H. Shakutsui, J. Phys. Chem. B 107 (2003) 2171–2173.
- T. Hirakawa, K. Yawata, Y. Nosaka, Appl. Catal. A: Gen. 325 (2007) 105–111.
- N. Bowering, G.S. Walker, P.G. Harrison, Appl. Catal. B: Environ. 62 (2006) 208–216.
- T. Ohno, K. Tokieda, S. Higashida, M. Matsumura, Appl. Catal. A: Gen. 244 (2003) 383–391.
- K. Sehested, H. Corfitzen, H.C. Christensen, E.J. Hart, J. Phys. Chem. B 79 (1975) 310–315.
- M. Roder, L. Wojnarovits, G. Foldiak, Radiat. Phys. Chem. 36 (1990) 175–176.
- E.L. Williams, D. Grosjean, Environ. Sci. Technol. 24 (1990) 811–814.
- T.N. Obee, R.T. Brown, Environ. Sci. Technol. 29 (1995) 1223–1231.
- G. Oberdörster, Z. Sharp, V. Atudorei, A. Elder, R. Gelein, W. Kreyling, C. Cox, Inhal. Toxicol. 16 (2004) 437–445.
- T. Noguchi, A. Fujishima, P. Sawunyama, K. Hashimoto, Environ. Sci. Technol. 32 (1998) 3831–3833.
- C. Feiyan, S.O. Pehkonen, M.B. Ray, Water Res. 36 (2002) 4203–4214.